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**Department of Energy**

Richland Operations Office

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DEC 09 1996



Ms. Donna L. Powauke  
Environmental Restoration/  
Waste Management  
Nez Perce Tribe  
P.O. Box 365  
Lapwai, Idaho 83450-0365

Dear Ms. Powauke:

RESPONSES TO COMMENTS FROM THE NEZ PERCE TRIBE ON THE DRAFT IN SITU REDOX MANIPULATION FIELD INJECTION TEST REPORT - HANFORD 100-H AREA, JUNE 1996, PACIFIC NORTHWEST NATIONAL LABORATORY, RICHLAND, WASHINGTON

Attached are the U.S. Department of Energy, Richland Operations Office (RL) responses to comments from the Nez Perce Tribe (NPT), Department of Environmental Restoration and Waste Management, on the Draft In Situ Redox Manipulation (ISRM) Field Injection Test Report - Hanford 100 Area, June 1996. Comments on this report were received in a letter from Ms. D. L. Powauke, NPT to Ms. D. Wanek, RL, "Review of Draft In Situ Redox Manipulation Field Injection Test Report" dated July 21, 1996, and where applicable, the test report has been modified to incorporate these comments. 44825

The referenced letter from the NPT also conveyed concerns regarding the behavior of uranium during and following the ISRM treatability test. Although experiments being conducted by the Pacific Northwest National Laboratory are not yet concluded, a progress report on the column studies and a transport modeling simulation of any released uranium are attached for your information.

If you have any questions, please contact me at (509) 373-9631.

Sincerely,

Arlene C. Tortoso, Project Manager  
Groundwater Project

GWP:ACT

Attachments

cc w/o attachs:  
J. S. Fruchter, PNNL  
A. J. Knepp, BHI

cc w/attachs:  
L. E. Gadbois, EPA  
W. W. Soper, Ecology

Effects of Dispersivity on Instantaneous Release of Reduced Uranium

November, 1996

Numerical modeling of groundwater transport of uranium was used to investigate a worst-case scenario for the instantaneous release of concentrated uranium during the re-oxygenation of a reduced zone in an aquifer. A one-dimensional advection-dispersion model was developed, based on parameters from the 100-D Area, to investigate the migration of the uranium plume for a distance up to 1000 m downgradient from the zone. This distance is the approximate groundwater path length from the proposed location of the ISRM at the 100-D Area (near well 199-D5-15) to the Columbia River.

Many of the important transport parameters (dispersivity, effective porosity, groundwater velocity) have not been adequately characterized for this area, but conservative estimates and ranges were selected for this study. The hydraulic parameters used are summarized in Table 1. Hydraulic conductivity varies over the groundwater path. A weighted average was used to calculate the average groundwater velocity over the path that was used in the model.

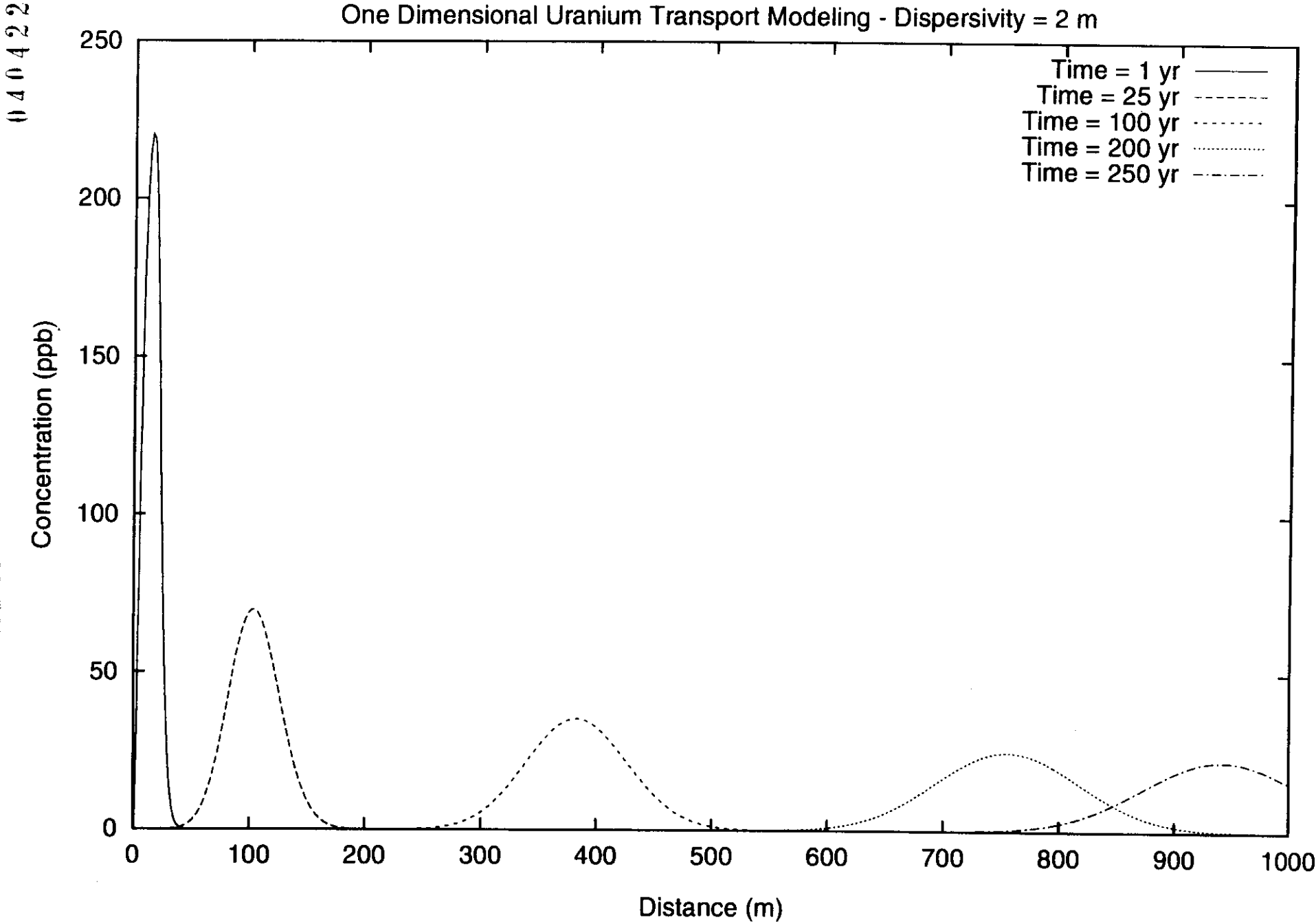
The study assumed that 85 pore volumes of groundwater with a uranium concentration of 2.7 ppb were concentrated in a 20 m wide reduced zone during 30 years of natural gradient flow. This concentrated uranium plume (230 ppb) is then released from the 20 m wide zone in one pore volume. The  $K_d$  used for uranium for this study was  $0.6 \text{ cm}^3/\text{g}$ , an average for the Hanford Site. This  $K_d$  results in a retardation factor of 7.4.

Results of the modeling are shown in the attached figures. These results show the concentrations at fixed points for three different values of dispersivity and at two different groundwater flow rates. Overall, the results show that significant attenuation occurs for the uranium plume by dispersion over the flow path and the resulting plume is reduced from the peak concentration of 230 ppb in the reduced zone to less than 13% of the peak value at a distance of 1000 m, the distance from the proposed site to the Columbia River.

Parameter	Value
Darcy Flux	0.015 m/day
Porosity	0.20
Pore Water Velocity	0.075 m/day
Bulk Density	$2.12 \text{ g/cm}^3$
$K_d$	$0.6 \text{ cm}^3/\text{g}$
Retardation Factor	7.4
Dispersivity	1 m, 2 m, 4 m

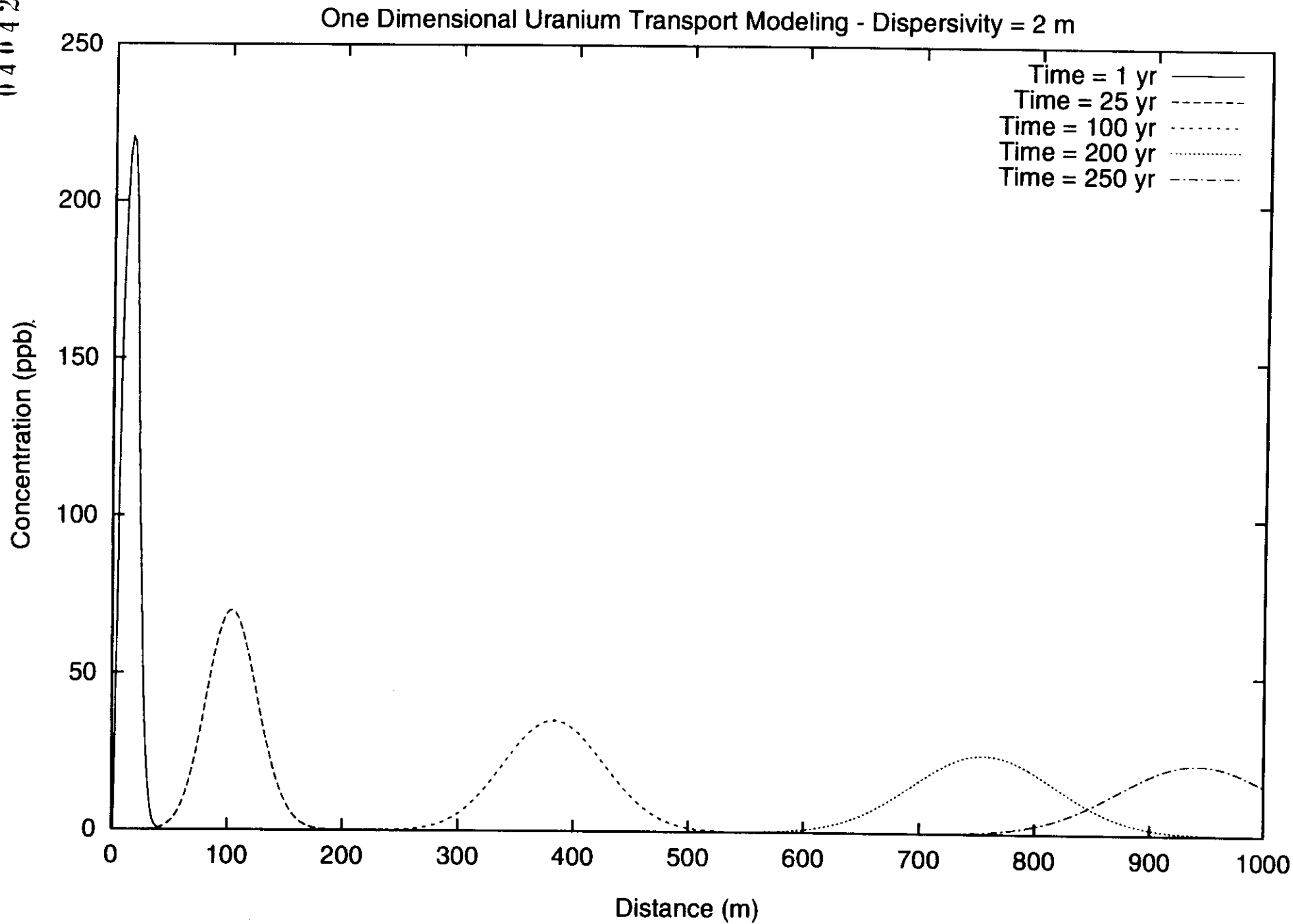
Simulation	Peak Concentration (ppb) at x=1000 m
D=1 m	28 ppb
D=2 m	22 ppb
D= 4 m	15 ppb
D=2 m, Flow Rate is 2X	22 ppb

One Dimensional Uranium Transport Modeling - Dispersivity = 2 m



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## U(VI) Behavior in Dithionite Reduced Sediments

November, 1996

A column experiment was conducted to determine the transport behavior of  $\text{UO}_2^{2+}$  through sediments reduced by dithionite. The column experiment was conducted in duplicate (two columns). The columns were composed of glass with an inside diameter of 2.5 cm, a length of 10 cm, and a volume of 49.1  $\text{cm}^3$ . The columns were filled with Hanford sediments collected from the 100-H Area. The porosity was measured to be 20.4 %. The sediments in the columns were first reduced by pumping a solution containing 0.1 M  $\text{Na}_2\text{S}_2\text{O}_4$ , 0.4 M  $\text{K}_2\text{CO}_3$ , and 0.4 M  $\text{KHCO}_3$  through the column at a flow rate of 3.6 pore volumes per day (1.5 ml/hr) for 25 hours. The columns were then allowed to sit for two days and then the reducing solution was flushed with groundwater collected from the 100-H Area. After flushing with 3.6 pore volumes of groundwater (24 hours at 1.5 ml/hr), the experiment was started. 100-H Area groundwater spiked with 10 ppb of  $\text{UO}_2^{2+}$  was pumped through each of the columns at 1.5 ml/hr. Uranium concentrations in the influent and effluent samples were measured with laser phosphorimetry.

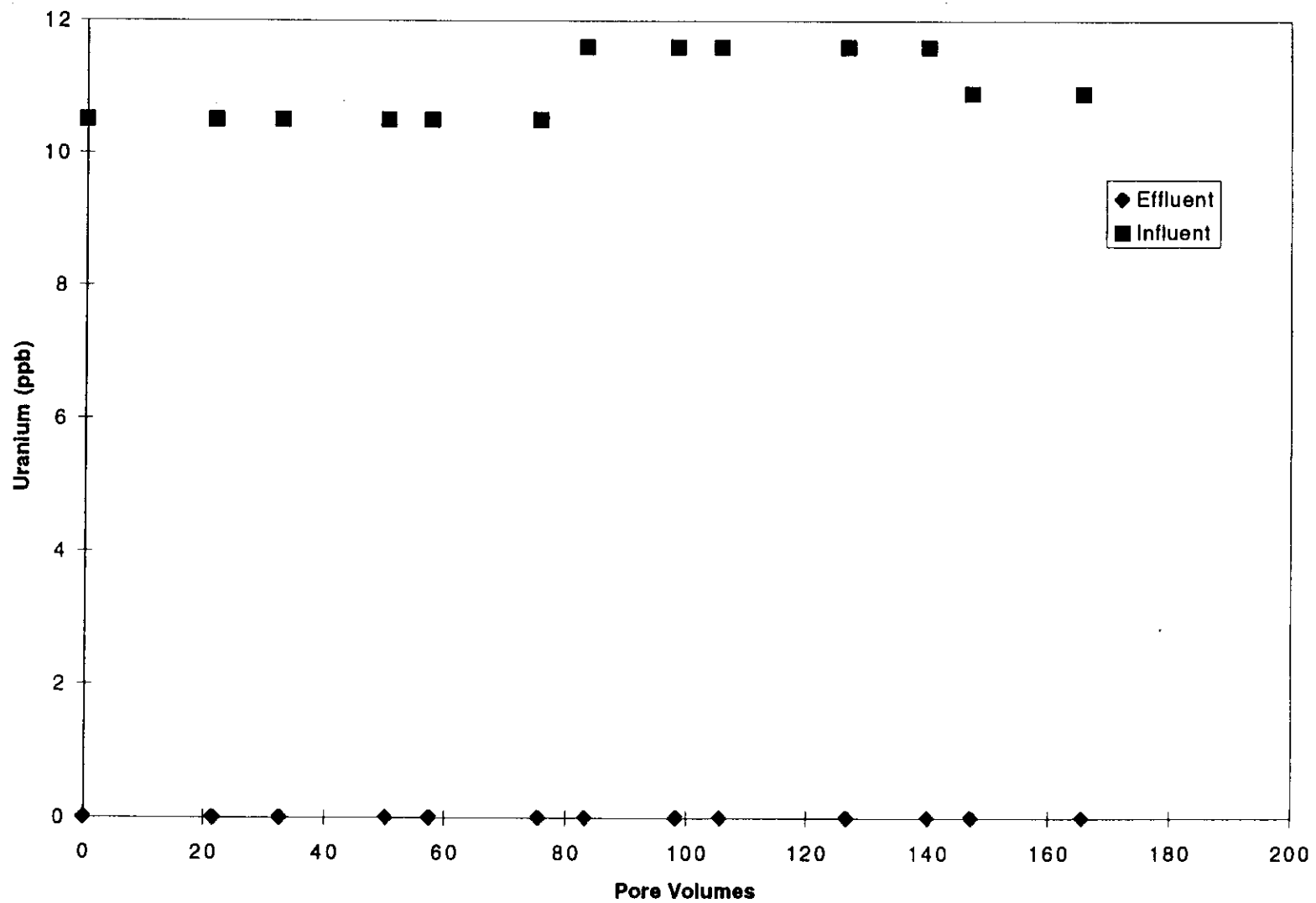
Based on previous measurements of the reductive capacity of dithionite reduced sediments (determined with an  $\text{O}_2$  reoxidation method) it was estimated that the sediment should have a reductive capacity of approximately  $7.4 \pm 5.6$  meq/kg. Based on the weight of material in each column (0.103 kg), the reductive capacity of each column should be approximately 0.76 meq. If we assume the oxygen concentration in the influent is 8 mg/l (1.0 meq/l), it was estimated that 0.76 liters (76 pore volumes) of groundwater would be required to reoxidize each column.

### Results

A total of 1656 ml (166 pore volumes) of solution was pumped through each column. Samples were collected at various intervals during the course of the experiment. At no time during the experiment was any uranium detected in the effluent of the column. The results are shown on the accompanying figure.

Oxygen measurements conducted during the experiment indicated that the dithionite reduced sediment was reducing only a small portion of the incoming oxygen at the relatively high column flow rate. As a result, it was apparent that the kinetics of oxygen reduction by dithionite reduced sediments is much slower than the reduction of uranium and chromate. Because the reduction of oxygen is so slow, it was determined that approximately 2000 pore volumes of solution would have to be pumped through the column at current velocities to reoxidize the column completely. This would require more than a year to complete the experiment. Other methods of reoxidizing the column are being investigated.

# Uranium Behavior in Dithionite Treated Hanford Sediments



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## Responses to General Comments

1. **The potential for mobilization of uranium:** We agree that care must be taken in siting a permeable redox zone so that it is not situated in areas of high groundwater uranium concentrations. However, the potential for mobilizing significant concentrations of uranium after reoxidation of the reduced zone are expected to be low at the 100D Area. There is no known plume of groundwater uranium contamination at 100D (Dresel et al., 1993, Hanford Site Groundwater Monitoring for 1993, PNL-10082, UC-402,403). The background concentrations of uranium in the groundwater in the Hanford unconfined aquifer are low (average 2.7 ppb, DOE/RL-96-61, Draft A, 1996). This will result in a maximum of only 200 grams of uranium being deposited on the 150 foot wide by 10 foot thick barrier during its thirty year life. Even if the attenuated uranium is released fairly quickly, and not controlled by solubility or sorption phenomena, the potential for damage is small. If the uranium accumulated from the 85 pore volumes treated during the thirty year assumed barrier life is released in a single pore volume, the concentration in this small plume would be 230 ppb. Transport calculation results (see attached report entitled Effects of Dispersivity on Instantaneous Release of Reduced Uranium, November 1996) indicate that the released uranium plume would be diluted by at least a factors of 7 to 10 by dispersion by the time it reached the Columbia River 3000 (1000m) feet from the site.

PNNL has been performing a series of column experiments to test the potential for uranium concentration and release on dithionite treated Hanford soils. Due to slower than expected reoxidation kinetics of the dithionite treated sediments, the columns have not reoxidized in the six weeks that the columns have been running. Current calculations show that it might be as much as a year before complete reoxidation of the 10 cm columns occur using oxygen saturated groundwater. Although this slow oxidation limits the utility of the column experiments, it should be a favorable attribute for the actual barrier in the field. PNNL is considering alternative methods for reoxidizing the columns, such as the introduction of ozone. However, this accelerated reoxygenation may not mimic the results in the field accurately. Progress to date is detailed in an attached report entitled U(VI) Behavior in Dithionite Reduced Sediments, November 1996.

2. **Reduction of hydraulic conductivity:** As noted in our reply in the section below on specific comments, the cause of the reduced hydraulic conductivity in the well bores is believed to be localized to the sandpack surrounding the monitoring wells. There is no evidence from other test results of a general decrease of hydraulic conductivity in the formation.

3. **Achievement of test objectives:** All objectives of the 100H Redox Field Test, as stated in the Test Plan for the 100H Area Redox Manipulation Experiment (August 1995), sections 2.2 and 2.3, were successfully met by the test to the degree possible during a one year period of evaluation. It was only intended to be a proof of principle demonstration. The concerns expressed by the Nez Perce Tribe will be covered by objectives of the proposed 100D Area Test Plan.



4. **Alternative redox manipulation methods:** Injection of reduced colloids into the aquifer is still in the bench-testing phase. It is possible that they will be an improvement. If such is the case, they will be substituted in the field test. The current schedule does not call for an injection of reducing agents at the proposed 100D site until FY 1998, so there is time to evaluate alternative methods.
5. **Results of uranium experiments:** See attached report for progress to date.
6. **Cost Information:** Under a separate project at Los Alamos National Laboratory, an analysis of the costs of this technology is being performed. This analysis is part of a continuing project supported at Los Alamos by DOE EM-50 to perform comparative cost analyses for innovative technologies. The results will be preliminary. The type of data necessary for an accurate cost analysis will be developed during the proposed treatability test at 100D. The results of this preliminary study are expected before the end of the first quarter of FY 1997, and will be publicly available. We will happy to supply the Nez Perce Tribe with copies.

#### Responses to Specific Comments

##### **Page 1.1, Paragraph 6:**

Yes, the term downgradient is more appropriate here.

##### **Page 1.2, Paragraph 2:**

A. It is true that the Redox Manipulation Zone, as configured for the proposed treatability test at the Hanford 100D Area may not be appropriate for the treatment of uranium. The statement in the introduction of the report was meant to apply more generically to the redox manipulation concept in general. For example, in a more favorable location, it could be used to concentrate the uranium in advance of other treatment, such as excavation or solution mining. Because chromate is the target contaminant for our DOE project, these additional uses of redox manipulation have not been studied.

B. Studies with long-lived radionuclides such as technetium, neptunium and plutonium have become prohibitively expensive due to the many requirements and regulations applying to this type of research. It is, in any event, not the intent of the present project to place redox barriers into regions of the Hanford unconfined aquifer which contain substantial amounts of these radionuclides without considerable advance research. Selenium and tin are already being examined in our trace metal mobilization studies. We will determine the feasibility of adding molybdenum to our studies in the future.

##### **Page 3.3, Last Paragraph, and Figure 1.4:**

The heterogeneity of the subsurface is one of the chief complications in all proposed groundwater remediation schemes, whether ex situ or in situ. However, pumping on the aquifer greatly exacerbates this problem. Therefore, it is the project's contention that permeable barriers, which rely on the natural groundwater gradient to move the contaminants to the treatment, are an

improvement. It is one of the major objectives of the proposed 100D Treatability Test to determine the effects of subsurface heterogeneity on the integrity of a linear barrier.

**Page 4.6, Paragraph 3:**

Because of the high hydraulic conductivity of the aquifer, the cone of depression formed during the withdrawal phase was relatively small (i.e., 1.8 ft at a radial distance of 5 ft and 0.5 ft at a radial distance of 23 ft), and of short duration (i.e., the cone of depression was developed during the four day withdrawal phase and recovered to static conditions in approximately the same amount of time). Monitoring of both wells and cores after the field test has not revealed any effects resulting from this short duration exposure of this part of the reduced zone.

**Page 10.2, Paragraph 6:**

The 10% impurity in the injected reagent was sodium sulfite.

**Page 10.4, Paragraph 2:**

X-ray diffraction (XRD) analysis shows it to be largely calcite ( $\text{CaCO}_3$ ).

**Page 10.15, Paragraph 4:**

As discussed below (Page 12.1, Paragraph 2 comment response), the "near well" reduction in permeability is most likely associated with the entrapment of suspended or colloidal material in the sandpack zone immediately outside the well screen during the withdrawal phase of the experiment. Because most of the mobile ferrous iron was removed during the withdrawal phase of the experiment, as indicated by post-experiment iron data at the site and the percent of the reagent and tracer recovered during the withdrawal phase of the experiment, precipitation of solubilized iron downgradient of the reduced zone is not expected to have a significant adverse effect on formation permeability.

**Page 10.15, Paragraph 6:**

Section 10.8.1, as presented in the draft report, was misleading and has been rewritten for the final draft. Well H5-1B is not located within the reduced zone (i.e., it saw less than 1% of the average dithionite concentration) but instead is located on the downstream edge of the reduced zone. The observed increase in dissolved oxygen concentration at H5-1B, and the other downgradient monitoring wells (H5-12, H5-13, and H5-14), are most likely associated with historically high Columbia River stage caused by heavy precipitation during the winter and spring of 1996, and the subsequent rise in the water-table beneath the 100-H Area. These abnormally high water-levels have increased dissolved oxygen levels in the upper part of the aquifer and may have altered the direction of the hydraulic gradient at the site.

**Figures 10-2 to 10-5:**

We agree that sulfur species concentrations are important. However, due to funding limitations, these analyses could not be completed in time for inclusion in the draft report. In September, additional funding was identified and samples from the withdrawal phase of the experiment were submitted for sulfate/sulfite analyses by ion chromatography. The total sulfur species recovery curve was well correlated with conductivity measurements made on the extraction stream during the withdrawal phase of the experiment (see the withdrawal phase conductivity data in Figure 10-2). A linear regression analysis of the total sulfur species concentration data and field measured conductivity data, using the method of least squares, resulted in an  $R^2$  value of 0.97. Based on integration of the extraction stream concentration data, it was estimated that 87% of the injected sulfur mass was recovered during the withdrawal phase. The total sulfur species recovery curve will be added to Figure 10-2.

**Table 10-6:**

Characterization of the impact of dithionite on microbial populations was limited to aerobic organisms for 2 reasons. First, aerobic bacteria are generally more sensitive to dithionite exposure and would better reflect the impact of treatment on resident populations. Second, the number of anaerobic bacteria in the Hanford unconfined aquifer is too small to detect with reasonable confidence.

**Page 12.1, Paragraph 1:**

See response number three in the above section that addresses general comments contained in the body of the letter.

**Page 12.1, Paragraph 2:**

As discussed in Section 10.7 and Appendix D, preliminary analysis results indicate the presence of a small zone (e.g., 1 in. to 4 in.) of reduced permeability immediately outside the wellbore. The cause of this zone of reduced permeability is unknown, but may be attributed to entrapment of suspended or colloidal material in the sandpack zone immediately outside the well screen during the pumpback phase of the experiment. This near well reduction in permeability caused no adverse effects during the injection or withdrawal phases of the field experiment and is not expected to result in any significant degradation in the overall hydraulic performance of the treatment zone.

Also as discussed in Section 10.7, a direct comparison of the pre- and post-experiment slug interference responses was not possible because of the change in aquifer thickness that occurred between the two test times. To eliminate the uncertainties associated with this change in aquifer thickness, additional slug interference tests will be conducted at the ISRM test site once water-levels have returned to their pre-experiment conditions. This second phase of hydraulic testing will provide a direct, and more definitive, comparison.

**Page 13.2, Section 13.4 and 13.5:**

See response number four in the above section that addresses general comments contained in the body of the letter.

**Page C.5, 100H Water Table Map:**

This water table map was taken directly from DOE-RL 1993. The problem may be associated with the recorded precision of the water-level measurements at each well location.

**Table E-2:**

See response to comment from Page 1.2, Paragraph 2.